

Evaluation of the chemical stability of some membranes in vanadium solution

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The chemical stability of Daramic[®], modified Daramic[®] and several commercial ion exchange membranes was studied in the vanadium redox battery (VRB). The Selemion[®] CMV membrane showed the lowest chemical stability in the VRB, while Nafion[®] 112 and New Selemion[®] (type 2) showed excellent stability. The composite membrane prepared by crosslinking of Daramic[®] with divinylbenzene (DVB) showed good chemical stability similar to the Selemion[®] AMV membrane. Sulfonation of the composite membrane and AMV membrane did not improve their stability in the vanadium solution. It was found that the weight loss of the membranes is almost proportional to the conversion of V(v) ions to V(IV) ions in the test solution showing that the chemical degradation is associated with the oxidation of the polymeric membrane material by the V(v) ions in the positive half cell electrolyte. The Nafion[®] 112 membrane was found to be susceptible to fouling which can be reversed by simply soaking in H₂SO₄ solution.

1. Introduction

Redox flow systems are based on the use of two fully soluble redox couples that are electrochemically oxidized and reduced at inert electrodes separated by a selective membrane.

The two half cell electrolytes stored in separate tanks outside the cells stack are circulated through the stack using pumps. The function of the membrane/separator is to prevent cross mixing of the positive and negative electrolytes, while allowing the transport of ions to complete the circuit during the passage of current. The VRB has shown energy efficiencies as high as 90% in 1 kW prototype stacks and possesses many features which make it ideal for large scale energy storage. One of the critical components for the successful commercial development of this system however, is the membrane.

Modification of low cost separators to impart permselective properties could lead to significant cost reduction for the production of a commercial redox flow battery. The microporous separator, Daramic[®], is widely used in the lead–acid battery due to its low cost and its chemical stability in sulfuric acid solution. However, without modification, it is unsuitable for the VRB due to high permeability leading to low coulombic efficiencies. Composite membranes were thus prepared by crosslinking of Daramic[®] with DVB and energy efficiencies of up to 74% were obtained [1]. Sulfonation of the composite membrane was also carried out to enhance their ion exchange capacity, as was modification of a commercial anion exchange membrane, AMV membrane (Asahi Glass Company,

Japan), so as to reduce the amount of water transport across the membranes [2].

Previous studies showed that Selemion[®] CMV membrane (Asahi Glass Co., Japan) exhibits very poor chemical stability, while Selemion[®] AMV membrane (Asahi Glass Co., Japan) shows good chemical stability when employed in the vanadium battery [3]. For this reason, the CMV and AMV membranes were used in the present study for comparison of the chemical stability of a range of other membranes. Daramic[®], composite Daramic[®], sulfonated composite Daramic[®], sulfonated AMV, Nafion[®] 112 (E.I. Du Pont, U.S.A.) and New Selemion[®] (type 2) (Asahi Glass Co., Japan) membranes were employed for long term chemical stability tests. The New Selemion[®] (type 2) is an anion exchange membrane not commercially available at present but was provided by Asahi Glass Co. for evaluation.

2. Experimental details

2.1. Composite Daramic[®] membrane preparation

Composite Daramic[®] membranes were prepared by the following method: a piece of Daramic[®] (size: 12 cm × 14 cm) was soaked for 12 h in a solution of DVB (40%) and ethanol (60%). The soaked Daramic[®] was transferred to a reactor in which distilled water and sodium persulfate were heated at 95 °C. Sodium persulfate was used as an initiator for polymerization of DVB. The temperature was increased to 98 °C in 10 minutes and the reaction allowed to take place for either 1 or 3 h [1].

The composite Daramic[®] was then sulfonated to produce the sulfonated composite membranes. The

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sulfonation treatment was also applied to the AMV membrane so as to modify its permeation properties. To incorporate strong cation exchange groups into the membranes, sulfonation was carried out using high concentration sulfuric acid at different temperatures of 60 °C or 80 °C for 24 h. Silver sulfate was used as a catalyst (1% w/w) for the sulfonation reaction [2].

2.2. Membrane characterization

The area resistance and the permeability of the membrane were evaluated by the methods described by Grossmith *et al.* [4]. For the permeability measurement, the diffusion coefficient of V(IV) ions across the membrane was determined. The membrane was exposed to a solution of 1 M VOSO₄ in 2 M H₂SO₄ on one side and a solution of 1 M MgSO₄ in 2 M H₂SO₄ on the other side. MgSO₄ was used to equalize the ionic strengths of the two solutions and to minimize the osmotic pressure effects. For the area resistance measurements, the membrane was exposed to a solution of 2 M VOSO₄ in 3 M H₂SO₄ on both sides.

The water transport across the membranes was evaluated by the method described by Hoong Ang [5]. Negative and positive half cell electrolytes at 50% state of charge (SOC) (1 M V(II) + 1 M V(III) on one side and 1 M V(IV) + 1 M V(V) on the other side) were used to evaluate the water transport behaviour of the composite membranes. An osmotic cell consisting of two symmetrical compartments, separated by the membrane under evaluation, was employed for this experiment. The tube connected to each compartment had an internal diameter (ID) of 4.25 mm, so each 7.05 cm change in height for both sides was equivalent to 1 ml solution transfer from one side to the other. Generally, for cation exchange membranes, the solution transfer is from the negative half cell to the positive halfcell of the VRB. The solution transfer for anion exchange membranes and nonselective membranes is however from the positive side to the negative side [3].

The ion exchange capacity (IEC) of the membranes was evaluated by the method described by Wycisk and Trochimczuk [6]. The membrane in the Na⁺ form was soaked in 1 M HCl solution to convert it to the H⁺ form. The membrane was then immersed in a known volume of 0.05 M KOH solution for 48 h at room temperature. The amount of H⁺ (in millimoles) was determined by back titration with a 0.05 M HCl solution. The membrane in the Cl⁻ form was soaked in 1 M KOH solution to convert it to an OH⁻ form membrane. This was then immersed in a known volume of 0.05 M HCl solution for 48 h at room temperature. The amount of OH⁻ (in millimoles) was determined by back titration with a 0.05 M KOH solution. The membrane was then washed with distilled water and dried under vacuum. The IEC was calculated as the ratio of the amount of H⁺ or OH⁻ to the weight of the dried membrane.

The vanadium redox cell used in the long term charge/discharge tests was a three-cell stack employing 2 M V(II)/V(III) and V(IV)/V(V) redox couples in H₂SO₄, with graphite felt electrodes and graphite plates as current collectors. The electrode and membrane area were 138 cm² and 160 cm², respectively, while the volume of the electrolytes was 300 ml for each halfcell. The cell was charged and discharged at a constant current density of 20 mA cm⁻².

Three different techniques were employed to evaluate the long term chemical stability of the membranes. Daramic[®], composite membrane, sulfonated composite membrane, CMV, AMV, sulfonated AMV, Nafion[®] 112 and Selemion[®] (type 2) membranes were exposed to a dilute solution of 0.1 M V(V).

For the preparation of the composite membrane, the polymerization reaction time of three hours was employed. The sulfonated composite membrane was prepared by sulfonation of the composite membrane at 60 °C for 24 h. A preweighed sample of each membrane (0.30 g) was soaked in 25.0 ml of 0.1 M V(V) solution prepared by dilution of the fully charged positive half cell electrolyte. Oxidation of the membrane by the V(V) ions leads to the formation of the blue V(IV) species which can be used as an indicator to measure the stability of a particular membrane. The concentration of V(IV) ions in the solution was thus determined by ultraviolet absorption spectrometry, using a Varian Super Scan 3 ultraviolet visible spectrophotometer. The absorbance of each solution was periodically determined to monitor the rate of oxidation by V(V). In order to compare the stability of each membrane when employed in the vanadium redox battery, the experiment was repeated using a constant area (10.5 cm × 5.0 cm) of each sample exposed to 25 ml of the V(V) solution.

To standardize the method, mixtures of 0.1 M V(IV) solution (prepared by dilution of the fully discharged positive half cell electrolyte) and 0.1 M V(V) solution were prepared with different ratios. The absorbance was determined for each mixture using a 0.1 M V(V) solution as reference for all measurements. The absorbance of each mixture was determined at a wavelength of 760 nm at which the maximum absorbance of V(IV) ions takes place [5].

In the second technique, the composite Daramic[®], the sulfonated composite Daramic[®], sulfonated AMV, Nafion[®] 112 and New Selemion[®] (type 2) membranes were exposed to a 2.0 M V(V) solution which is the fully charged positive halfcell electrolyte of the VRB. In the preparation of the composite membranes, polymerization times of either one or three hours were used for crosslinking of Daramic[®] with DVB. The composite Daramic[®] and AMV membranes were also sulfonated in 98% H₂SO₄ at 60 °C for 24 h. A piece of each membrane (10 cm × 10 cm) was placed in 40 ml of the V(V) solution and the area resistance, V(IV) permeability and IEC values were periodically measured.

In the last technique, the sulfonated composite membrane, Nafion[®] 112 and New Selemion[®] (type 2)

membranes were simultaneously employed in a VRB three-cell stack which was subjected to continuous charge/discharge cycling at 20 mA cm^{-2} and their area resistance and diffusivity measured periodically. The Daramic[®] was first crosslinked with DVB for 3 h followed by sulfonation in 98% H_2SO_4 at 60°C for 24 h to prepare the sulfonated composite membrane used in this test. Fouling of these membranes was also studied by monitoring any increase in area resistance with time during charge/discharge cycling.

Morphological studies were undertaken with a field emission scanning electron microscope (FES-EM), Hitachi S-900. X-ray dispersion analysis were also carried out using a Jeol JXA-840 scanning microanalyser and a Link An 10000 EDAX (energy dispersive X-ray analyser).

3. Results and discussion

The absorbance of the various solutions containing different ratios of V(v) and V(iv) species and a total vanadium concentration of 0.1 M , was determined at 760 nm and a plot of absorbance vs percentage V(iv) is shown in Fig. 1. The absorbance of the mixture increases linearly with increasing % V(iv) showing that Beer's law is obeyed for these solutions. When the same weight of each membrane was exposed to each of the V(v) solutions, the absorbance against time plots of Fig. 2 show that the rate of V(iv) appearance is highest in the case of the CMV membrane which has the poorest chemical stability. This confirms earlier studies [3], that CMV membrane has poor chemical stability when employed in the VRB. On the other hand, Nafion[®] 112 and New Selemion[®] (type 2) shows excellent stability in the V(v) solution as indicated by the low rate of increase in V(iv) absorbance in Fig. 2. Although, Daramic[®] shows acceptable chemical stability compared with CMV membrane, much better chemical stability is observed after modification of Daramic[®] to produce the composite Daramic[®] and the sulfonated composite Daramic[®] membranes. The composite Daramic[®] shows similar stability to the AMV membrane which has already been shown to have acceptable life in the VRB [3]. This can be attributed to the formation of

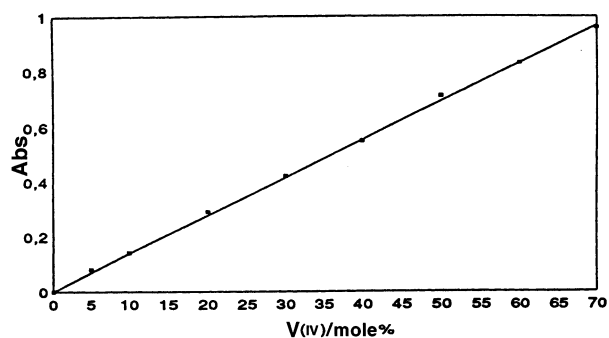


Fig. 1. Ultraviolet absorbance at 760 nm against V(IV)% for different ratios of V(v) and V(iv) ions (total vanadium concentration = 0.1 M)

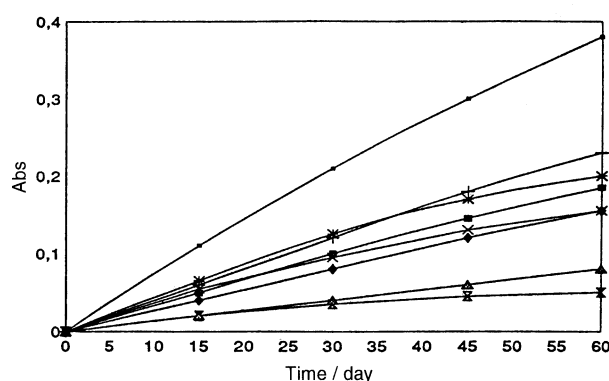


Fig. 2. Change in absorbance at 760 nm of 0.1 M V(v) solutions in which different membranes have been soaked for two months: (■) CMV, (+) Daramic[®], (*) sulfonated composite Daramic[®], (■) sulfonated AMV, (x) composite Daramic[®], (◆) AMV (Δ) New Selemion[®] (type 2), and (⊗) Nafion[®] 112.

poly(DVB) layers on both sides of Daramic[®] after crosslinking [1].

The chemical stability of the sulfonated composite Daramic[®] and the sulfonated AMV membranes was found to be slightly poorer than that of the composite Daramic[®] and the AMV membranes, respectively. Because of the destructive nature of the sulfonation process, the poly(DVB) layers become thinner after sulfonation [2]. This degradation of the membrane during sulfonation would thus be responsible for their lower chemical stability compared with the corresponding unsulfonated membranes.

Each of the membranes was also weighed after two months soaking in 0.1 M V(v) solution and a quantitative analysis of the results is presented in Table 1. As expected, some weight loss is observed for most of the membranes when exposed to the oxidizing V(v) solution. When the CMV membrane was soaked in the solution for two months, 27% of the V(v) ions in the solution were reduced to V(iv) ions, and as a result of the membrane oxidation, 0.14 g of its initial weight was lost. The Nafion[®] 112 and New Selemion[®] (type 2) membranes showed zero weight loss after two months, in agreement with the very low conversion of V(v) to V(iv) (3% and 5%, respectively). The weight loss of 0.07 g for Daramic[®] and

Table 1. Quantitative analysis of the chemical stability of various membranes

Membrane	Final weight /g	Membrane area /cm ²	Reduction of V(v) to V(iv) /%
CMV	0.16	21.5	27
Daramic [®]	0.23	25.5	16
Sulfonated composite Daramic [®]	0.25	23	14
Sulfonated AMV	0.26	22.7	13
Composite Daramic [®]	0.27	22.2	11
AMV	0.28	25.1	11
New Selemion [®] (type 2)	0.30	52.5	5
Nafion [®] 112	0.30	31.5	3

Initial weight = 0.30 g

Table 2. The results of chemical stability evaluation of various membranes

Membrane	Initial wt /g	Final wt /g	Wt loss /mg cm ⁻²	Wt loss /%	Reduction of V(v) to V(IV) /%
CMV	0.73	0.40	6.28	45.2	66
Daramic®	0.62	0.48	2.67	22.6	33
Sulfonated Composite Daramic®	0.68	0.56	2.28	17.6	32
Sulfonated AMV	0.69	0.59	1.90	14.5	30
Composite Daramic®	0.71	0.64	1.33	9.8	26
AMV	0.63	0.59	0.76	6.3	23
Nafion® 112	0.50	0.49	0.19	2	5
New Selemion® (type 2)	0.30	0.30	0	0	5

Exposed area = 52.5 cm²

0.02 g for the AMV membrane is almost proportional to the conversion of V(v) ions to V(IV) as seen in Table 1.

Since these membranes have different thickness and densities, in the above tests, which employed constant membrane weight, different sample areas were involved. For better comparison of their relative stability in the vanadium redox battery, therefore, the experiment was repeated with the same area of each membrane soaked in the V(v) solution. The results are presented in Table 2. As expected, the poorest chemical stability was again observed for the CMV membrane which shows twice the rate of V(v) reduction as the Daramic®. Among the tested membranes, the CMV membrane has the highest weight loss value of 1.4×10^{-2} g cm⁻², while the New Selemion® (type 2) has the lowest value of 5.7×10^{-3} g cm⁻².

In the second part of this study, composite Daramic®, sulfonated composite Daramic®, sulfonated AMV, New Selemion® (type 2) and Nafion® 112 membranes were separately soaked in the 2.0 M V(v) solution for six months and their area resistance and

permeability periodically evaluated. The results are presented in Tables 3 and 4. Table 3 shows the results obtained for composite Daramic® and sulfonated composite Daramic® membranes prepared by crosslinking with DVB for either 1 or 3 h. The area resistance of the samples prepared by crosslinking for 1 h reduced by 58%, while that of the composite Daramic® and the sulfonated composite Daramic® membranes crosslinked for 3 h, reduced by 32% and 25%, respectively, after six months soaking in the 2.0 M V(v) solution. Previous studies have shown that the greater the crosslinking reaction time, the thicker the poly(DVB) layers on both sides of composite membrane. As expected, thicker layers would offer more protection against oxidation. However, as seen in Fig. 3, the decrease in area resistivity and increased vanadium permeability after exposure to V(v) solution can be attributed to the partial destruction of membrane's polyethylene backbone due to the oxidation reaction.

Field emission scanning electron microscopy (FESEM) was used to study the morphology of the

Table 3. Area resistivity and diffusivity of composite Daramic® and sulfonated composite Daramic® membranes before and after soaking in the 2.0 M V(v) solution

Membrane	Crosslinking reaction time /h	Soaking time /day	R /Ω cm ²	10 ⁴ Ks /cm min ⁻¹
Composite Daramic®	1	0	1.56	4.15
		60	1.31	4.93
		120	1.16	5.51
		180	0.99	6.06
Composite Daramic®	3	0	2.68	2.15
		60	2.35	2.63
		120	2.12	2.97
		180	2.03	3.11
Sulfonated composite Daramic®	1	0	1.39	4.27
		60	1.12	5.18
		120	0.94	5.91
		180	0.88	6.43
Sulfonated composite Daramic®	3	0	2.52	1.53
		60	2.31	2.17
		120	2.14	2.56
		180	2.01	2.81

R: Area resistance

Ks: Diffusivity

Daramic[®] and composite Daramic[®] membranes before and after soaking in the 2.0 M V(v) solution. Chromium was used to coat the composite membrane samples but since photographs of Daramic[®] samples coated with chromium were not clear, gold was employed to coat these samples. The photograph may thus show a slightly different surface from the real surface, as chromium particles are much finer than gold particles.

In general, the photographs show that soaking in the V(v) solution leads to the partial destruction of the polyethylene structure of the Daramic[®]. The pores on the surface of the soaked Daramic[®], Fig. 3(b), are larger than those on the surface of the

unsoaked Daramic[®], Fig. 3(a). Cross-sectional micrographs of composite membranes before and after soaking are also different. Thin surface layers formed on both sides of the Daramic[®] after crosslinking [1], (seen in Fig. 3(c)), could not be observed after soaking. However, as seen in Fig. 3(d), poly(DVB) particles remain in the pores of the membrane, explaining the higher stability of the composite Daramic[®] in the 2.0 M V(v) solution.

The IEC of the sulfonated composite membranes was also evaluated after samples had been soaked in the V(v) solution for six months. For the membrane initially crosslinked for 1 h this value decreased from 1.80 to 1.39 mmol g⁻¹ of dried membrane (mmol dg⁻¹)

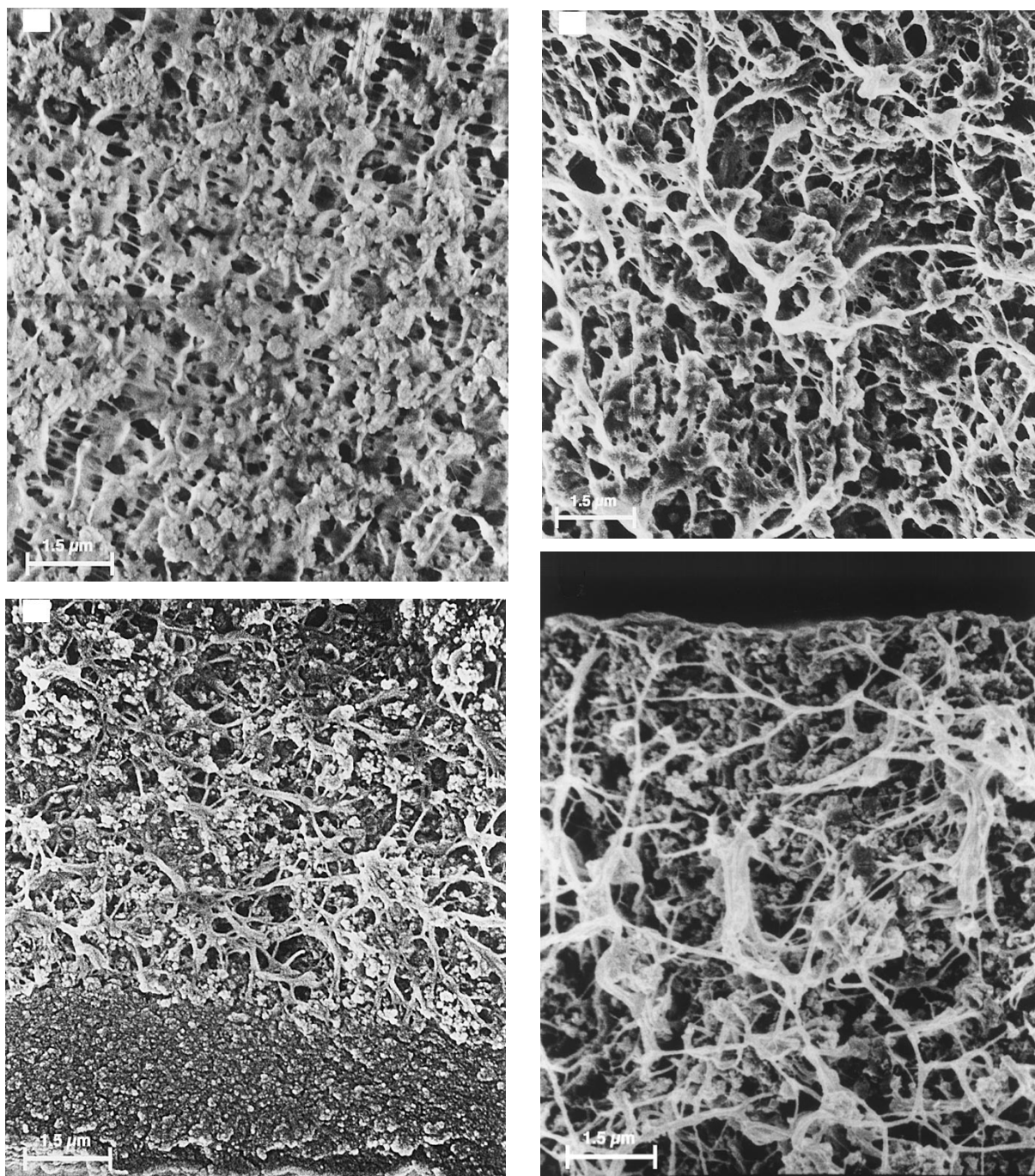


Fig. 3. FESEM micrographs of (a) Daramic[®] (surface), (b) Daramic[®] after six months soaking in 2.0 M V(v) solution (surface), (c) composite Daramic[®] (cross section) and (d) composite Daramic[®] after six months soaking in 2.0 M V(v) solution (cross section).

(representing a 22.8% decrease), while for the membrane initially crosslinked for 3 h, this value reduced from 2.35 to 1.77 mmol dg⁻¹ (corresponding to a 24.7% decrease in IEC).

Water transport across the sulfonated composite membrane initially crosslinked for 3 h was also measured after three and six months soaking in the V(v) solution. The results are presented in Fig. 4. Water transfer measurements across the composite Daramic[®] and the sulfonated composite Daramic[®] membranes before soaking in the V(v) solution are also presented for comparison. In the case of the sulfonated composite membrane the water transport is seen to increase with increasing soaking time and is believed to be associated with the corresponding reduction in IEC. However, the amount of water transferred across the same membrane after six months soaking in the V(v) solution was still less than that across the unsulfonated composite membrane which had zero IEC.

From Table 4, it can be observed that both the area resistivity and diffusivity of the sulfonated AMV membrane also reduced after soaking in the V(v) solution. Partial annihilation of the butadiene backbone and anion exchange groups may be responsible for the former, while destruction of cation exchange groups incorporated during sulfonation may cause the latter. The area resistance and diffusivity of the unsulfonated AMV membrane were 2.80 Ω cm² and 3.20×10^{-6} cm min⁻¹, respectively.

Table 4 also shows that the area resistance of both the Nafion[®] 112 and New Selemion[®] (type 2) membranes decreased slightly after soaking in the V(v) solution, while their diffusivity showed a slight increase. The IEC of the Nafion[®] 112 membrane remained constant at 1.35 mmol dg⁻¹ before and after six months soaking. In this case, destruction of the perfluorinated backbone would be insignificant. On the other hand, the IEC of the New Selemion[®] (type 2) membrane decreased from 1.85 to 1.57 mmol dg⁻¹ after six months soaking. These results show that both membranes have good to excellent stability in the V(v) solution which is consistent with the results obtained by the first technique (Tables 1 and 2).

In the last part of this study, the sulfonated composite Daramic[®], the New Selemion[®] (type 2) and

Table 4. Area resistivity and diffusivity of sulfonated AMV, New Selemion[®] (type 2) and Nafion[®] 112 membranes before and after soaking in the 2.0 M V(v) solution

Membrane	Soaking time /day	R / Ω cm ²	10 ⁴ Ks /cm min ⁻¹
Sulfonated AMV	0	2.54	3.85
	60	1.72	2.68
	120	1.76	1.71
	180	1.79	1.01
New Selemion [®] (type 2)	0	0.98	1.16
	60	0.93	1.34
	120	0.88	1.50
	180	0.71	1.88
Nafion [®] 112	0	0.89	1.77
	60	0.84	1.87
	120	0.78	1.98
	180	0.68	2.07

R: Area resistance

Ks: Diffusivity

the Nafion[®] 112 membranes were employed in the small three-cell VRB stack for charge/discharge cycling. The cell was charged and discharged continuously for over 1950 cycles at a constant current density of 30 mA cm⁻² and the area resistance and diffusivity of the membranes evaluated after two months and six months of continuous cycling. Table 5 shows that the area resistance and diffusivity of the sulfonated composite membrane and the New Selemion[®] (type 2) membrane remained almost constant after the long term charge/discharge cycling showing that these membranes are not susceptible to fouling when employed in the VRB. The area resistance of the Nafion 112 membrane increased, however, while its diffusivity decreased after the long term charge/discharge cycling of the cell, suggesting that this membrane may be susceptible to fouling in the VRB.

To study whether this fouling is reversible, the Nafion 112 membrane samples which had been cycled for 60 and 180 days in the VRB were removed and soaked in 2 M H₂SO₄ solution for three weeks and their area resistance and diffusivity periodically measured. The results presented in Table 6 show that the area resistance of the membrane decreases and

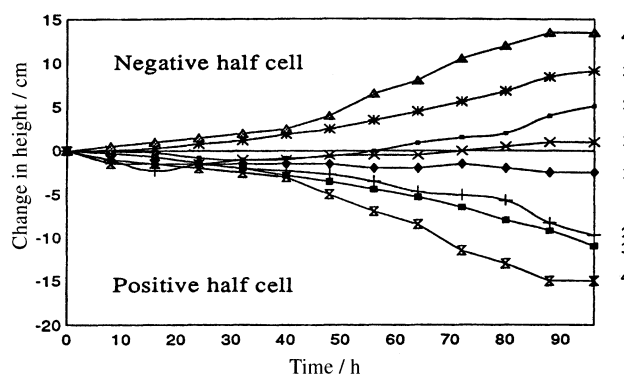


Fig. 4. Transport of water across (x, \blacklozenge) sulfonated composite Daramic[®] (\blacksquare , +) sulfonated composite Daramic[®] after three months soaking in 2.0 M V(v) solution, (\times , \blacksquare) sulfonated composite Daramic[®] after six months soaking in 2.0 M V(v) solution and (Δ , \times) composite Daramic[®], for vanadium electrolytes of 50% initial SOC. Symbols refer to (negative, positive) halfcell, respectively.

Table 5. Area resistivity and diffusivity of sulfonated composite Daramic[®], New Selemion[®] (type 2) and Nafion[®] 112 membranes before and after long time charge/discharge cycling

Membrane	Cycling time /day	R / Ωcm^2	$10^4 K_s$ /cm min ⁻¹
Sulfonated composite Daramic [®]	0	2.52	1.53
	60	2.35	2.07
	180	2.21	2.34
New Selemion [®] (type 2)	0	0.98	1.16
	60	0.96	1.17
	180	0.91	1.19
Nafion [®] 112	0	0.89	1.77
	60	1.40	1.25
	180	1.88	0.89

R: Area resistance

Ks: Diffusivity

almost attains its original value after soaking in the H₂SO₄ solution for 2–3 weeks.

Elemental analysis of the Nafion[®] 112 membrane samples before and after cycling and after soaking in H₂SO₄ solution was carried out to further investigate the fouling of the membrane in the VRB. The samples were coated with carbon before analysis. The result for the Nafion[®] 112 membrane before cycling showed the presence of sulfur from the sulfonic groups and silica in the membrane. The elemental analysis of the Nafion[®] 112 membrane after six months cycling showed the presence of vanadium and zinc, confirming the fouling of the membrane due to the partial blockage of the membrane pores by vanadium and zinc which occurs as an impurity in the vanadium solution. However, the elemental analysis of the sample after three weeks soaking in 2.0 M H₂SO₄ solution showed that both vanadium and zinc peaks disappeared. It can thus be concluded that Nafion 112[®] is susceptible to reversible fouling when employed in the VRB and that the original properties can be restored by soaking in H₂SO₄ solution.

4. Conclusion

Of the membranes tested in the present study, the Selemion[®] CMV membrane showed the lowest che-

mical stability in the VRB, while Nafion[®] 112 and New Selemion[®] (type 2) showed excellent stability in 0.1 M V(v) solution. Daramic[®] was found to be twice as stable as the CMV membrane in the V(v) solution, however, much better chemical stability was observed for the composite Daramic[®] membrane which was prepared by crosslinking of Daramic[®] with DVB. Sulfonation of the composite Daramic[®] and the AMV membranes led to a slight decrease in their chemical stability.

The weight loss of the membranes tested was found to be almost proportional to the conversion of V(v) ions to V(IV) ions in the test solution showing that the chemical degradation is associated with the oxidation of the polymeric membrane material by the V(v) ions in the positive half cell electrolyte of the VRB.

The composite Daramic[®] and the sulfonated composite Daramic[®] membranes which had been crosslinked with DVB for 3 h were found to be more chemically stable than those crosslinked for only 1 h. The water transport properties of the sulfonated composite membrane were determined immediately after preparation and after the sample had been soaked in 2.0 M V(v) solution. An increase in the water transfer after soaking is believed to be associated with the corresponding reduction in IEC of the membrane. However, the amount of water transferred across the sulfonated composite membrane after six months soaking in the V(v) solution was still less than that across the unsulfonated composite membrane. The area resistivity and diffusivity of the sulfonated AMV membrane reduced after soaking in the V(v) solution showing that the membrane oxidizes to some extent in the V(v) solution. In the case of Nafion[®] 112 and New Selemion[®] (type 2) membranes however, soaking in the V(v) solution led to only a slight reduction in area resistance, while their diffusivity increased slightly. This confirms that both membranes show negligible oxidation in the V(v) solution.

Long term charge/discharge cycling tests in the VRB showed that the area resistance and diffusivity of the sulfonated composite Daramic[®] and New Selemion[®] (type 2) membranes remained almost constant after six months. While these membranes are not susceptible to fouling when employed in the VRB, the results showed that area resistance of the Nafion[®] 112 membrane increased, while its diffusivity decreased after long term charge/discharge cycling. This membrane is thus susceptible to fouling in the VRB, but this fouling can be reversed by simply soaking in H₂SO₄ solution.

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Table 6. Area resistivity and diffusivity of Nafion[®] 112 membrane before and after soaking in the 2.0 M H₂SO₄ solution

Sample	Cycling time /day	Soaking time /day	R / Ωcm^2	$10^4 K_s$ /cm min ⁻¹
Nafion [®] 112	60	0	1.40	1.25
		7	0.97	1.35
		14	0.92	1.55
		21	0.90	1.70
Nafion [®] 112	180	0	1.88	0.89
		7	1.43	1.13
		14	0.92	1.54
		21	0.90	1.71

R: Area resistance

Ks: Diffusivity

photographs from the Electron Microscopy Unit, University of NSW and V. Piegeroua for the electron dispersive analysis from the school of Materials Science and Engineering, University of NSW.

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